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Microwave Plasma Detoxification Process for Hazardous Wastes. Phase II Systems Application Evaluation

Lockheed Missiles and Space Co, Inc, Palo Alto, Calif

Prepared for

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Microwave Plasma Detoxification Process for Hazardous Wastes

Phase II. Systems Application Evaluation

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This preliminary survey has revealed new information on several highly toxic substances which exist within the continental U.S. for which there is no satisfactory means of disposal. They exist in multiple ton quantities, as well as small centigram batches at a multitude of locations. They are, specifically, materials in search of a disposal method, such as the microwave plasma detoxification process (MWP). These materials which have been surveyed for suitability in the MWP include the following exceedingly dangerous compounds and mixtures:

- o Cancer-causing nitrosamines, vinyl and vinylidene chlorides, dioxin-containing organohalogens, and aromatic amine compounds which heretofore have been considered only as oddities, or as being present only in small quantities.
- o Acute-toxicity organometallic compounds and heavy metal complexes, such as mercury, arsenic, cadmium, and lead compounds, derived from industrial processes and pesticides.
- o Nerve-poisons from military sources, which include organophosphorus chemicals stock-piled above ground, and from pesticide wastes which are only slightly less hazardous.

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MICROWAVE PLASMA DETOXIFICATION PROCESS FOR HAZARDOUS WASTES

Phase II. Systems Application Evaluation

by

L. J. Bailin
Lockheed Palo Alto Research Laboratory
LOCKHEED MISSILES & SPACE COMPANY, INC.
Palo Alto, California 94304

Contract No. 68-03-2190

Project Officer

Donald A. Oberacker
Solid and Hazardous Waste Research Division
Municipal Environmental Research Laboratory
Cincinnati, Ohio 45268

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This report summarizes a broad spectrum of applications for microwave plasma processing of hazardous and highly toxic wastes. Technical discussions at U.S. EPA Headquarters, regional offices, national conferences on toxic waste disposal, and at other government and industrial facilities contributed to the information on the diverse substances which could be disposed of by treatment with this new method.

Francis T. Mayo
Director
Municipal Environmental Research
Laboratory

ABSTRACT

This preliminary survey has revealed new information on several highly toxic substances which exist within the continental U.S. for which there is no satisfactory means of disposal. They exist in multiple ton quantities, as well as small centigram batches at a multitude of locations. They are, specifically, materials in search of a disposal method, such as the microwave plasma detoxification process (MWP). These materials which have been surveyed for suitability in the MWP include the following exceedingly dangerous compounds and mixtures:

- Cancer-causing nitrosamines, vinyl and vinylidene chlorides, dioxin-containing organohalogens, and aromatic amine compounds which heretofore have been considered only as oddities, or as being present only in small quantities.

- Acute-toxicity organometallic compounds and heavy metal complexes, such as mercury, arsenic, cadmium, and lead compounds, derived from industrial processes and pesticides.

- Nerve-poisons from military sources, which include organophosphorus chemicals stock-piled above ground, and from pesticide wastes which are only slightly less hazardous.

Identification of these materials and sources is abstracted in Table A.

This information was obtained to identify real-world industrial requirements and applications for microwave plasma detoxification of high-toxicity waste streams and chemicals. To obtain the data, technical discussions were held at six U.S. EPA regional offices, U.S. EPA Office of Solid Waste, Washington, DC, plus other government and industrial facilities. Two national conferences on toxic waste disposal were also attended.

With respect to identities, techniques, and locations of hazardous wastes, the U.S. EPA regional offices, although highly cooperative, did not have a good "handle" on the exact quantities of materials. The national conferences also left many questions unanswered on this problem. It was indeed surprising to learn after much time spent how poor the data were on quantities as related to specific locations. Only estimates, at best, could be made. And for military-type materials, it may be stated unequivocally, that a more extensive survey will be needed for their identification and location. It was frustrating to know that the materials were "out there," but not be able to learn anything beyond that point.

Positive information of a type, however, was expressed at the national meetings which dealt with the philosophy of safe disposal. One group or faction spoke of incineration as the only genuine means for decomposition or destruction. Landfill, however, was loudly promulgated by those who regarded incineration as too difficult

to control for highly toxic materials, and thus too costly, dangerous, etc. The incineration partisans described the storage and landfill alternative as only a temporary answer; in this instance, the substances are covered up underground and left for future generations to be troubled with.

If one wishes to consider, therefore, the applicability of the microwave plasma technique as an ultimate disposal procedure, the materials cited in the table meet the process requirements eminently well. The process to date detoxifies low poundage quantities, depending on apparatus size, i.e., 1 - 10 lbs/hr in the original 5 kW unit, and 10 - 30 lbs/hr in the 15 kW unit which is undergoing tests now. Pending continued development, units of 50 - 100 lbs/hr are envisioned. Several of these in parallel should have sufficient capacity to satisfy all but very high volume throughput levels. Predicted costs per pound based on three 15 kW systems operating continuously is $0.20 - 0.25. Dilute toxic waste water streams are not suggested, only because the energy of the plasma would be wasted in producing a stream or water plasma rather than producing the chemical reactions which are necessary for total detoxification. However, concentration of these streams can be accomplished, and these would then be candidates for the microwave plasma process. Thus, the MWP appears as an important adjunct, or the only method in many instances, for the detoxification of hazardous wastes, which, because of their "too-hot-to-handle" reputations, cannot be buried in landfill, or moved across statelines for detoxification or disposal.

This report fulfills Phase II of Contract No. 60-03-2190 by the Lockheed Palo Alto Research Laboratory, Lockheed Missiles & Space Company, Inc., under the sponsorship of the U.S. Environmental Protection Agency. The period covered was February - July 1977.

TABLE A. IDENTITIES AND KNOWN SOURCES OF

Toxic Material	Classification
Organophosphorus Compounds:	
• Nerve gases or G-agents (phosphonofluoridates)	Anticholinesterase nerve toxin
• Flame retardant (e.g., "Tris")	Carcinogen
• Pesticides (phosphonates, thiophosphonates)	Anticholinesterase
Organometallic Compounds:	
• Arsenical pesticides	Lipoid toxin
• Mercurials pesticides	Primary organ toxins in humans
• Lead (tetraethyl lead)	" " " "
• Metal cyanides	" " " "
• Nickel carbonyl, Zn, Cd, Mn, Se, V, Misc. Heavy metal compounds	Primary organ toxins
Halogenated Compounds:	
• Hexachlorobenzene (containing dioxin) PCBs, Kepone, Mirex, etc.	Carcinogens
• DBCP (dibromochloropropane)	Male sterility in humans
• Vinyl and vinylidene chlorides	Carcinogens
Organonitrogen Compounds:	
• Nitrosamines (e.g., dimethyl nitrosamine)	Carcinogens, teratogens, mutagens
• Aromatic amines (e.g., benzidines)	"
• Polyaromatic hydrocarbons, PAH (dyes, pigments)	"

(a) LD_{50} < 100 (oral lethal dose 50% test animals, < 100 mg/1 kg body weight).
(b) Temporary method: Materials have not been rendered chemically or biologically safe.

HIGHLY TOXIC[a] AND HAZARDOUS SUBSTANCES WITHIN CONTINENTAL U. S.

Source of Material	Quantities and Location, Where Known	Disposal Method
Military: Stored pure agents. Stored waste streams. Stored neutralization products	Thousands of gallons Several thousand lb (Colorado, Utah, Maryland)	Storage[b] above ground " " "
Manufacturer	Probable 1000's of lb (California)	Unknown
Commercial, Industrial, Agricultural: Pesticide manufacturing wastes Outdated supplies Unlabeled, unknown supplies	1 to 10,000 lb in various locations	Chemical disposal sites, incineration
Commercial, Industrial, Agricultural: Solids Holding ponds (Alexandria, Va. area) New Mexico)	100's of lb 100 to 1000 gallons	Storage underground Storage above ground
Solids, solutions	100's of lb, gallons	Storage underground
Process wastes	1000's of lb (East and West Coast)	Storage above ground
Plating wastes, solids		Storage above and underground Wet oxidation, UV, ozonolysis
Petroleum catalysts, pesticides, experimental complexes	1 to 100 lb, a few 1000's of lb (Texas, California, New Jersey)	Storage above and underground
Commercial, Agricultural	1000's of lb	Storage above and underground, Incineration
Fumigant/agricultural chemicals	Estimated 1000's of lb (California)	Unknown
Industrial waste streams and process bottoms	Estimated 1000's of lb	Storage and incineration
Industrial, Hospitals, Universities, Cancer Centers. (Note: Expect larger quantities to be identified at university laboratories from greater awareness at these sources)	1 to 10 lb (throughout U.S.)	Storage above and below ground
	100's of lb	" " " "
U.S. Navy smokes, flares, etc.	100's of lb	Unknown

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The Project Officer for the Environmental Protection Agency was Mr. Donald A. Oberacker, Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, Cincinnati. His guidance and support are sincerely acknowledged.

Appreciation is also expressed to personnel from U.S. EPA Headquarters and regional offices mentioned in this report who contributed time and effort in aid of this program.

SECTION 1

INTRODUCTION

Of the approximately 10 million tons of toxic and hazardous wastes which are generated yearly in the United States, it has been estimated that 10 to 20% will need special methods for disposal. These materials are made up in large part from pesticides which have been withdrawn from use, obsolete or below-specification toxic substances, industrial wastes from chemicals, explosives, etc., and biological residues, carcinogens, mutagens, and related materials.[1]

For compounds of nominal toxicity, such as diluted DDT or other pesticides mixed with solvent or municipal sludges, on the order of LD_{50}'s of 500 or higher,[2] notable achievements have been accomplished in thermal destruction, chemical and biological detoxification, and special landfill methods. However, with the exception of incinerator processing, relatively little new technology has been developed within the last 10 years for the disposal of highly toxic, refractory, and extremely persistent wastes in the form of concentrates, pure chemicals, or nondiluted process wastes.

The technique of deomposition of hazardous, concentrated organic compounds by passage through a microwave discharge began at the Lockheed Palo Alto Research Laboratory in 1967. In a U.S. Army supported program conducted during 1970 - 1972, the decomposition of toxic gas simulants was carried out in which nearly 100% decomposition of selected organophosphonate materials was performed in a laboratory-size plasma system.[3] In 1975 - 1976, the U.S. EPA, Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, Cincinnati, Ohio, approved a feasibility study to test the process on several pesticides and toxic wastes. As the consequence of several highly successful evaluations, the construction of an expanded scale system followed, which resulted in an increase in throughput from 1 - 5 g/hr for the laboratory unit to 450 - 3200 g (1 to 7 lb) per hr in the larger system.[3] Consequently, the further design and construction of pilot equipment was authorized by the U.S. EPA for expansion to a portable unit of 5 to 14 kg (10 to 30 lb) per hr.

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(1) Report to Congress, Disposal of Hazardous Wastes, U.S. Environmental Protection Agency, Publication SW-115, 1974

(2) Lethal dose for 50% of test animals in mg/kg of body weight

(3) Bailin, L. J., M. E. Sibert, L. A. Jonas, and A. T. Bell, "Microwave Detoxification of Toxic Vapor Simulants," Environmental Science & Technology, 9(3), 254-58, 1975

(4) Bailin, L. J. and Barry L. Hertzler, "Development of Microwave Plasma Detoxification Process for Hazardous Wastes," Phase I, U.S. EPA-600/2-77-030, Apr 1977

Preliminary to the construction and testing of the new unit, it was considered essential to perform an intensive short-term survey to identify current industrial requirements and potential applications for the process for application to real-world highly toxic hazardous chemicals and waste streams. Those materials which might be detoxified and yield valuable by-products, such as organometallics, would also identified and proposed for additional development work. This report summarizes the information which was obtained in this study.

SECTION 2

SAE PROGRAM CRITERIA

To perform the systems application evaluation (SAE), specific tasks were prescribed, as follows:

1. Identify existing industrial requirements and potential applications for microwave plasma processing of real-world, highly toxic, hazardous chemicals and waste streams. Municipal, agricultural, and ordinary chemical wastes were not included.

2. Collect and publish the information and provide to U.S. EPA and related personnel who are directly concerned with toxic and hazardous waste management.

The method by which the information was obtained involved visits and technical interviews with cognizant personnel at U.S. EPA Headquarters and regional offices; attendance, participation, and discussion at two national conferences on toxic wastes; and additional discussions at local government and industrial facilities. Details of visits, interviews, presentations, etc. are given in the sections which follow.

SECTION 3

U.S. EPA REGIONAL OFFICE INTERVIEWS

Of the ten U.S. EPA regional offices, interviews were conducted with personnel from six locations.

Region	Location
I	Boston, MA
III	Philadelphia, PA
V	Chicago, IL
VI	Dallas, TX
VII	Kansas City, MO
IX	San Francisco, CA

The regions in which the 60 percent sampling was performed are shown on the map in Figure 1.

Preliminary to discussions of toxic problem wastes, a description of the microwave plasma system was presented by the interviewer using visual aids, including an 8-minute color-sound 16-mm movie. The information was concerned with current and projected process size, capacity, costs, and the anticipated schedule for scale-up. In this way, the applicability of the process to regional problems and specific hazardous substances could be estimated more readily.

REGION I, NORTHEAST

Boston, MA

Contact: Richard R. Keppler, (Acting) Director, Office of Research and Development

The materials of high toxicity to be disposed of were, principally, PCB's in the sludge bottoms of several Massachusetts rivers, and waste pesticides. The pesticides were estimated to be 200 tons at various locations throughout the region. The PCB's are present at 40 – 50 ppm in the river sludges; if the contaminant is not removed, the problem was estimated to remain approximately 50 years. See Table 1.

Toxic waste disposal is carried out mainly by means of storage and specialized incineration. Until better methods become available, these are the only procedures acceptable.

Figure 1. U.S. Environmental Protection Agency Regions and regional interview locations.

TABLE 1. HIGHLY TOXIC AND HAZARDOUS WASTE MATERIALS – U.S. EPA REGIONS I, III, IV

Source of Information	Location of Toxicants	Substance	Form	Quantities	Means of Disposal
U.S. EPA Region I (New England) ME, VT, NH, MA, RI, CT	Massachusetts: Acushnet River New Bedford Harbor Housatonic River	PCB's	River and bay sludge bottoms	40–50 ppm High tonnages	Storage; specialized incineration
	Entire region	Various pesticides	All forms	> 200 tons	Storage
U.S. EPA Region III (Middle Atlantic) PA, MD, DE, VA, WV	Hopewell, VA	Kepone	Powder, etc.	Estimated: 50 tons	None
	James River, VA	Kepone	River sludge	High tonnages	High-temperature incineration
	Arlington (Washington, D.C.)	Arsenical pesticide	Solids Holding ponds	Estimated: 100's of lb 100's of gal	Unknown
	Entire region	Cyanide and ferric cyanide from plating baths	Solution Solids	Estimated: 100's of gal 100's of lb	– –
	Belle, WV	Nitrosamines	Water solution	Estimated: 100's of gal	–
	Various locations	Vinyl chloride Vinylidene chloride		Estimated: tonnage quantity	–
U.S. EPA Region V (Midwest) NM, WI, IL, IN, OH, MI	New Albany, IN	Hexachlorobenzene	Liquid	Estimated: 100's of gal	Storage
	Entire region	PCB's	Liquid	Estimated: > 100's of lb	Storage and incineration
	Minneapolis, MN	Hexachloro-naphthalene in fuel oil	Liquid	Estimated: > 1000 gal	Storage
	Entire region	Organophosphonate pesticide		Estimated: > 100's of lb	Storage
	Michigan	Unlabeled chemical wastes	Liquids Solids	Several thousand 55-gal drums	Storage

REGION III, MIDDLE ATLANTIC

Philadelphia, PA

Contact: Albert Montague, Director, Office of Research & Monitoring

The following materials known to exist within the region were described as needing special disposal methods:

Organic arsenical pesticides, Arlington, Virginia (Washington, D.C. area). No disposal method exists other than chemical landfill.

Nitrosamines (carcinogens) present in cutting fluids were found in Belle, West Virginia, as a water contaminant, and in Baltimore, Maryland, as an air contaminant.

Cyanide effluents from plating baths, especially ferric cyanide, are problem areas. The latter is not oxidized readily by ozone or hypochlorite. Location is nonspecific, i.e., they occur wherever cyanide baths are used.

Vinylidene chloride and vinyl chloride wastes in several-ton quantities were located at one manufacturer's site.

Kepone and Kepone sludges at Hopewell, Virginia, are notorious problem materials. Contaminated sludge is present in high multiple ton quantities in the James River area. For Kepone pesticide solids stored in drums, a 50-ton figure was estimated. See Table 1.

REGION V, MIDWEST

Chicago, IL

Contact: Karl Bremer, Toxic Substance Coordinator

Discussion indicated that significant quantities of hexachlorobenzene, PCB's, hexachloronaphthalene in fuel oil, still-bottoms, organophosphonate pesticides, research chemicals, and several thousand 55-gallon drums of unlabelled chemical wastes are either being sent to landfills, or are being stored "outside" and "just rusting." See Table 1. It was agreed that some means must be found for final disposal, since the landfills are only storage areas for these highly toxic substances.

REGION VI, SOUTHWEST

Dallas, TX

Contact: Ms. Mildred Smith, Special Assistant for R&D Surveillance and Analysis

Several problems were discussed, principally those involving organometallic compounds. In Texas and New Mexico, several hundred pounds of arsenicals are being stored in warehouses for want of a better means of disposal. Experimental quantities of organometallic compounds in the 1 - 100 lb range which contain Gd, In, etc.,

have also been reported by petroleum companies to be in storage at their chemistry and catalyst laboratories. Nickel carbonyl, lead compounds, zinc and manganese salts are known toxic substances used by oil companies which need to be disposed of correctly. See Table 2.

It was reported that an inventory of toxic and highly toxic materials is being collected at this time by Region VI from industrial and other sources. It was estimated that data from this survey will be available on or about the latter part of 1978.

REGION VII, MIDWEST

Kansas City, MO

Contact: Morris Tucker, Chief, Solid Waste Programs

The principal hazardous materials of concern include:

Hexachlorobenzene mixed with oil, 4600 gallons, contaminated with 100 - 1000 ppm of p-dioxin (2, 3, 7, 8-tetrachlorodibenzo-p-dioxin), in a tank stored near St. Joseph, Missouri. No safe detoxification method exists.

PCB's and PCB-contaminated soil over a large area at relatively dilute concentrations are located in the St Louis, Missouri, area.

Pesticides in a fire-damaged warehouse in which the materials were partially destroyed, or consist of unlabelled containers, are being retained above ground in the St. Louis area. See Table 2.

REGION IX, WEST

San Francisco, CA

Contact: Charles T. Bourns, Chief, Solid & Hazardous Waste Management Program

Discussion revealed, principally, the problems in disposal of PCB's present in waste transformer oils and old or discarded capacitors, Kepone and similar pesticides, and miscellaneous organometallics. See Table 2. For details on quantities, referral was made to the California State Department of Health for information from their toxic substances list. These materials are identified in Section 5.

Inspection of both tables show the large numbers and varied types of toxic and hazardous wastes scattered across the continental United States. They cover all types of compounds, mixtures, etc., in all forms of matter. Based on the program scope, the search indeed identified many materials which need treatment as soon as possible. It is also quite certain that many more substances will be located under more intensive scrutiny – which is strongly suggested for future investigations.

TABLE 2. HIGHLY TOXIC AND HAZARDOUS WASTE MATERIALS – U.S. EPA REGIONS VI, VII, IX

Source of Information	Location of Toxicants	Substance	Form	Quantities	Disposal
U.S. EPA Region VI (Southwest) AR, LA, NM, OK, TX	Victoria, TX	Arsenicals	Solids	Several hundred pounds	Landfill or storage
	New Mexico	Arsenicals	Solids	Several hundred pounds	Landfill or storage
	Houston, TX	Nickel carbonyls Lead compounds Gd, In, Zn, Mn, Pb compounds	All forms	1–100 lb each	Landfill or storage
	Texas	Waste stream mixtures of organometallics	Liquid, Slurries	Estimated: 1000's of gal	Storage
U.S. EPA Region VII (Midwest) IO, KS, MO, NE	St. Joseph, MO	Hexachlorobenzene in oil (100–1000 ppm p-dioxin)	Liquid	5000 gal	Storage
	St. Louis, MO	PCB's	Liquid	> 100 gal	Storage
	St. Louis, MO	Pesticides	All Forms	> 1000 lb	Storage
U.S. EPA Region IX (West) CA, NV, AZ	Entire region	Kepone	Solids	Multipounds	Landfill (Class I sites)
	Entire region	Pesticides	All Forms	> 1000 lb	Landfill
	Entire region	Organometallics	All forms	> 100 lb	Landfill
	Entire region	PCB's	Liquid, Capacitors	Multigallons	Landfill Landfill

SECTION 4

NATIONAL MEETINGS ON TOXIC WASTE DISPOSAL

Two conferences were attended during the SAE program. At the first, an EPA-Lockheed coauthored paper was presented on the initial phase of microwave plasma process development. At the second, solutions to difficult residue disposal problems were presented by varied speakers. The primary objective of attendance by the writer was to develop a high degree of familiarity with the real issues of hazardous materials disposal and detoxification. In this regard, the goal was well met. There were, however, a number of presentations at the second conference which were, unfortunately, repetitions from the first.

1. NATIONAL CONFERENCE ABOUT HAZARDOUS WASTE MANAGEMENT

San Francisco, CA, February 1 - 4, 1977

Chairman: Dr. Harvey F. Collins, California State Department of Health

This meeting was sponsored by the U.S. EPA, California State Department of Health, and Governmental Refuse Collection and Disposal Association.

The EPA-Lockheed coauthored paper, "Developments in the Low Temperature Microwave Plasma Process for Hazardous Waste Disposal and Recovery" reported data obtained during the EPA, Cincinnati, supported program on the successful scale-up of the microwave plasma process. Additional relevant topics included

- Definitions of terms, such as hazardous, extrahazardous, highly toxic wastes, etc., in several independent contributions.

- Development of the California hazardous waste transportation manifest, its complexity and requirements, or "Getting Hazardous Waste From Here to There."

- Visits to two Northern California Class I (Chemical Disposal) Sites for the disposal of hazardous/toxic material: Pacific Reclamation and Disposal, Inc., Benecia, and Sierra Reclamation and Disposal, Inc., Martinez, CA. There were varied opinions on what highly toxic materials would be acceptable for disposal underground. For example, no military wastes, politically "hot" or related materials are accepted at Class I sites in California. Since incineration is extremely limited within the state, landfill appears to be the only acceptable means for disposal.

- With regard to landfill, encapsulation, etc., in the keynote address to the conference, Senator John F. Dunlap, Member of the California Legislature and author of California's 1972 Hazardous Waste Control Legislation, called for additional emphasis on recycling and recovery of energy values. Senator

Dunlap stated that toxic material burial, although acceptable now, may become a serious problem later. Paraphrasing his further remarks, he said, the undesirable storage of these substances underground may require guards-with-guns to watch over them – forever.

2. NATIONAL CONFERENCE ON TREATMENT AND DISPOSAL OF INDUSTRIAL WASTEWATERS AND RESIDUES

Houston, TX, April 26 - 28, 1977

This symposium, sponsored by AIChE (South Texas Section); Gulf Coast Waste Disposal Authority; U.S. EPA; University of Houston; and Information Transfer, Inc., dealt with, principally, the treatment of industrial wastewaters and residues with regard to solutions to difficult disposal problems, ultimate disposal (so-called encapsulation) treatment processes, costs of alternative methods, area-wide management, and new concepts.

The presentation included technical and administrative problems, which in the main, were concerned with sludge, pretreatment methods, and similar broad-based applications. Although toxic or highly toxic substances were discussed as part of a number of presentations, no new toxic materials not previously covered in other papers or publications were revealed. Important contributions were, however, made during several presentations and discussions, as condensed below:

- Dr. Stephen J. Gage, Deputy Assistant Administrator for Energy, Minerals and Industry, U.S. EPA, Washington, D.C. In the keynote address, he emphasized recovery and re-use. For example, metallic zinc was listed as an "endangered" material. He said that only 20 years of production remain within the U.S., and, therefore, diligent resource recovery should be practiced.

- Mr. George S. Thompson, Jr., Chief, Metals and Inorganic Chemicals Branch, IERL, Cincinnati, discussed the need for recovery of metals, especially toxic species, such as Hg, Cu, Pb, Cd, As, Se, and V from industrial sludges, incinerator discharges, etc.

No single method for disposal of toxic wastes was considered applicable for all types of materials. Indeed, there were several interesting informal discussions during and after the meeting "in the halls" regarding the difficulties associated with even the major disposal techniques. For example, incineration was stated as the only real method for decomposition or destruction. However, landfill was promulgated by those who regarded incineration as too difficult to control (for highly toxic materials), costly, dangerous, etc. Incinerator partisans described the storage and landfill alternatives as only a temporary answer in which the substances are covered up underground and left for future generations to be troubled with.

The information gathered at both meetings supported the proposal that organometallics, chlorinated hydrocarbons, and carcinogens are strong candidates for microwave plasma processing, but, of course, these toxins had been known previously. Support for the use of the plasma process was derived from the estimated quantities of the materials to be detoxified, although the exact numbers were not known with confidence by any of the meeting personnel contacted.

SECTION 5

OTHER GOVERNMENT AND INDUSTRIAL INTERVIEWS

Referral of the interviewer to the California Department of Health (CDH), Berkeley, by EPA Region IX; a return visit by a CDH waste management specialist to Lockheed Palo Alto Research Laboratory (LPARL); and a visit to Arthur D. Little, Inc. (ADL), Cambridge, MA, comprise the interviews listed in this section.

1. CALIFORNIA STATE DEPARTMENT OF HEALTH

Berkeley, CA

Contact: Warren Manchester, Associate Industrial Hygienist, Waste Management Division

A visit to the Waste Management Division yielded maximum information on the toxic materials which the State of California classifies as extremely hazardous, i.e., those with an oral, rat LD_{50} (lethal dose, 50% fatalities) of less than 50 (< 50 mg toxicant/1 kg body weight of test animal). A briefing on these materials indicated that literally hundreds of highly toxic materials, in quantities from 1 - 10 g to thousands of gallons, are being sent to Class I chemical disposal sites. The location of these sites in California is shown in Figure 2. These included PCB's, pesticides, carcinogens, organometallics, cyanides, antibiotics, rocket fuels, hydrofluoric acid, and rejected or distressed substances. These are part of one-time laboratory clean-outs, monthly industrial waste inputs to the sites, hospital biological wastes, and local, city government disposals from their pesticide and rodenticide storage. A summary tabulation of materials deposited at the sites since 1975 is listed in Table 3. During the visit, the applicability of the microwave plasma detoxification process to these wastes was discussed, particularly since Class I landfill has been the only answer for disposal of many of these highly toxic materials within the state.

All the items in Table 3 are candidates for detoxification by the microwave plasma process.

2. CALIFORNIA STATE DEPARTMENT OF HEALTH

Berkeley, CA

Contact: Carl G. Schwarzer, Waste Management Specialist, Vector & Waste Management Section

As the result of the discussion at Berkeley on the applicability of the microwave plasma process to many of the toxic wastes now being sent to Class I sites, a return visit by a CDH specialist to the Lockheed Palo Alto Research Laboratory was arranged. The purpose was to discuss in greater detail the start-up date of the 15-kW plasma

1. PACIFIC RECLAMATION & DISPOSAL
2. SIERRA RECLAMATION & DISPOSAL. NO LONGER OPERATING.
3. RICHMOND SANITARY SERVICE
4. HOLLISTER DISPOSAL SITE
5. SIMI VALLEY LANDFILL
6. CALABASAS LANDFILL
7. PALO VERDES LANDFILL
8. WEST COVINA LANDFILL
9. STRINGFELLOW QUARRY COMPANY. NOW CLOSED.
10. OMAR RENDERING COMPANY
11. OTAY LANDFILL
*CLASSIFIED AS ACCEPTABLE FOR DISPOSAL OF GROUP I WASTES BY THE CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARDS.

Figure 2. Extremely hazardous waste Class I disposal sites in State of California.

TABLE 3. TYPES OF EXTREMELY HAZARDOUS WASTES SENT TO CALIFORNIA CLASS I LANDFILL SITES – 1975 – 1977

Materials	Source	Form	Quantities
Alkali Cyanide	Plating company	Solution, 1 lb/gal	2000 gal/yr
PCB's	Transformer manufacturer	Liquid, transformer oil	62 × 55 gal drums
		Liquids	40 × 55 gal/yr
Nickel Cyanide	Plating company	Solution, 12 oz/gal	3000 gal/yr
Sodium Cyanide	Plating company	Solution, 12 oz/gal	800 gal/yr
Tetraethyl Lead	Petroleum company	Sludge	1000 gal
Aflatoxin	USDA	Contaminated peanut butter, 1000 ppm	2 × 55 gal drums
Arsine Mixed With Nitrogen	Semiconductor company	Gas, 5000 ppm	Bottles under pressure
Benzidine Hydrochloride	Hospital	Solid	225 g
Strichnine	Plant nursery	Solid, gopher poison, 3% agent	350 lb
Rocket Fuels/ Propellants/ Miscellaneous		Solids	10-lb batches
α-Naphthylamine	Chemistry laboratory	Solid	100 g
Methyl Yellow	Hospital	Solid	20 g
Agricultural Chemicals. Outdated: Organophosphonates, Chlorinated Hydrocarbons, and Carbomates	Supply house	Solids, dispersions	500–1000 g
Antibiotics, Miscellaneous	Hospital	Solids, dispersions	lb quantities

unit, the estimated costs, and, specifically, the potential for handling chemical carcinogens, such as benzidine, nitrosamines, etc. Part of Mr. Schwarzer's responsibility is to reduce as far as possible the influx of these and related toxic materials to the Class I sites. A second visit is scheduled when the 15-kW system becomes operational.

3. ARTHUR D. LITTLE, INC.

Cambridge, MA

Contact: Dr. Joan Berkowitz

In 1975 - 76, A. D. Little, Inc. (ADL) performed a survey study for U.S. EPA, Office of Solid Waste, Washington, D.C., under EPA Contract 68-01-3554, to evaluate new disposal methods for toxic wastes. A visit to ADL was made in order to correct what Lockheed believed to be a misunderstanding on ADL's part concerning the engineering aspects of the microwave plasma process. Personnel at ADL had had previous experience with these plasmas, but were not familiar with the recently developed, EPA, Cincinnati, supported Lockheed microwave scale-up program. In this context, several subjects were discussed, which included: microwave plasma chemistry and its engineering potential as applied to hazardous wastes, the background of the LPARL plasma process scale-up, and the application of an oxygen plasma as the principal reactor medium. By the completion of the discussions, the misunderstandings were cleared-up, such that the projected Lockheed scale-up plans for the near future were understood readily by the meeting participants. Potential toxic materials discussed for MWP treatment were nitrosamines, carcinogens, organophosphonate nerve poisons, chlorinated hydrocarbons, and organometallic compounds.

SECTION 6

FORUM ON MICROWAVE PLASMA PROCESS
U.S. EPA, WASHINGTON, D.C.

The purpose of the forum was to present to interested individuals within the Government environmental community the most recent developments in microwave plasma technology for the disposal of very hazardous wastes. The attendees represented EPA, NIH, Army, Air Force, Navy, and the Frederick Cancer Research Center. The presentation was held March 1977 at the Office of Solid Waste (OSW), Waterside Mall Headquarters. Mr. Donald A. Oberacker, Solid and Hazardous Waste Research Division, Cincinnati, presided as EPA meeting chairman. Dr. L. J. Bailin, Lockheed principal investigator, presented the technical data.

As the result of a broad line of questions posed and answered during a well-attended and lengthy session, several conclusions were reached, which may be summarized, principally, as follows.

- OSW appeared convinced with regard to the workability and usefulness of such a device, particularly portable units.

- Agencies other than EPA, such as NIH, the Army, and Air Force showed an appreciation for small, but highly toxic waste streams which need a disposal process, such as the microwave plasma, but for which costs are of secondary importance.

- A number of materials were brought forward which would be amenable to this treatment. These included organometallics (mercury, arsenic compounds), organophosphonates (anticholinesterase toxins), polyaromatic dyes and polyaromatic hydrocarbons (carcinogens). These were mentioned at various times as materials in search of a disposal method.

This meeting served, therefore, as a focal point for questions which had accumulated for more than a year since the inception of the program in April 1975. It served as a forum since various needs were expressed for the process, even though a complete cost analysis for a portable system was not available then. It emphasized that, although costs were without doubt important, there were materials which needed to be detoxified now for which no satisfactory means for disposal existed at "ten times the price."(5) Thus, as a result of the information exchange, important new information and needs were determined for microwave plasma processing within the governmental sphere. As an example, one agency requested that it be permitted to support the program in a related study during the continuing developmental phases. All the information obtained in the meeting was therefore scheduled for follow-up, since the requirement was immediate for the agency which stated this request.

(5) See Appendix for estimation of operating costs.

SECTION 7

CONCLUSIONS AND RECOMMENDATIONS

As the result of a Systems Application Evaluation, it has been shown that, without doubt, there are a large number of compounds, wastes, mixtures, and problem materials which need safe, efficient, and cost-effective means for disposal. Current methods have been almost exclusively underground landfill, or above-ground warehouse or exposed drum storage. This is not a true disposal, but a "hiding" action, in that the materials are still there, in place, waiting for a disposal method which will carry out the detoxification eventually.

The highly toxic and hazardous wastes which have been found applicable for microwave plasma processing, as determined on this program, include gases, pure liquids, solutions, slurries, pure solids, and solids mixed with inorganic components. These are stored in drums, cannisters, bottles, in dispersion, and in settled-out form, both pumpable and nonpumpable in consistency and, therefore, cover the gamut of materials handling technologies. The materials are listed by classification below.

- Organometallic compounds and waste pesticides, containing mercury, arsenic, cadmium, nickel, zinc, and other metals
- Organophosphorus compounds and wastes, such as chemical warfare agents and similarly constituted pesticides.
- Organic nitrogen compounds and wastes which have been shown to manifest significant carcinogenic, teratogenic, and mutagenic tendencies in test animals.
- Halogen-containing hydrocarbons and related impurities, which include many compounds of recent notoriety, such as PCB's, Kepone, p-dioxin, DBCP, etc.

All of these are problem materials which give great concern to those who are responsible for their safe disposal. This is so even for compounds which are present in gram or pound excesses, as well as for the hundreds of gallons/thousands of pounds of toxic chemicals.

Therefore, an important place as a true-disposal mechanism may be readily claimed for the microwave plasma process. The method is important, since it can be made portable for use in areas where the materials to be treated cannot be transported or moved because of local or federal ordinanaces regarding the handling of these substances. Also, the recovery of by-product metal values from the organometallic wastes would serve national needs by way of recycling, as described by EPA guidelines.

Therefore, recommendations concerning further process development from the point of view of need are positive. It should be noted, however, that although hundreds and thousands of pounds of these highly toxic materials have been listed, we did discover that the details on their many specific locations were woefully poor. It was indeed surprising to learn after much time spent how poor these data were. It was frustrating to know that the materials were "out there" but not be able to learn anything beyond that point. And for military-type toxic and hazardous materials, it may be stated unequivocally that a more extensive survey will be needed for their identification and location.

APPENDIX

ESTIMATED OPERATING COSTS FOR 15-kW MICROWAVE PLASMA SYSTEM

The costs for treating approximately 1 ton of Kepone solids/day are detailed below.

Equipment costs are based on current figures for microwave plasma hardware and predicted needs for ancillary parts. The trailer and truck are estimated separately.

Electrical usage, 1.6 kWh,* for operating the plasma system on a per pound treated basis, is estimated to be constant for all organic materials, since the maximum microwave power available from the power sources is used for generation of the plasmas.

Oxygen consumption for Kepone is 5.58 SCF/lb calculated, based on formation of chlorine, and equimolar quantities of CO_2 and CO.

A 330-day/yr, 24 hr operation is used, in which three units treat 90 lb/hr of Kepone solids. Throughput is 2,160 lb/day, or 712,800 lb/yr.

Labor costs are based on one-man operation of three automated units.

EQUIPMENT AND OPERATING COSTS

1. Microwave hardware, including vacuum pump, materials feed, recovery system, and on-board analyzer, per unit	$ 85,000
2. Cab and trailer, one per 3 MWP units	25,000
3. Electricity, industrial usage	$0.015/kWh
4. Oxygen, large volume usage Add $3,000/yr storage costs	$0.005/SCF
5. Labor	$9/hr

The calculated process costs based on these data are tabulated as follows:

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*Development of Microwave Plasma Detoxification Process, Phase I, EPA Report 600/2-77-030, April 1977, p. 30.

VARIABLE COSTS (YEARLY BASIS)

Operating labor, 7920 hr × $9/hr		$ 71,280
Maintenance, 4% of equipment, including cab and trailer		11,200
Oxygen, 712,800 lb × 5.58 SCF/lb × oxygen cost		22,887
Electricity, 712,800 lb × 1.6 kWh/lb × electricity cost		17,107
	A. Total Variable Costs	$122,474

FIXED COSTS

Capital Recovery (10 yr − 7%)*		39,872
Taxes and Insurance (2%/yr)		5,600
	B. Total Fixed Costs	$ 45,472
	Total Annual Costs, A + B	$167,946
	Treatment Cost per Pound	$ 0.23

*Compound interest factor, uniform series capital recovery, 0.1424, from D. G. Newman, Engineering Economic Analysis, Engineering Press, San Jose, 1976.